

AD-A183 449

LIQUID CRYSTALLINE COPOLYMERS OF MONOMER-PAIRS
CONTAINING MESOGENIC UNITS. (U) CASE WESTERN RESERVE
UNIV CLEVELAND OH DEPT OF MACROMOLECULAR

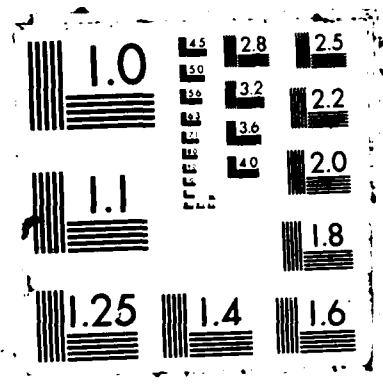
1/1

UNCLASSIFIED

V PERCEC ET AL. 1987 TR-13 N00014-86-K-0284 F/G 7/3

NL





DTIC FILE COPY

(12)

AD-A183 449

OFFICE OF NAVAL RESEARCH

Contract N00014-86-K-0284

R&T Code 413c024---01

Technical Report No. 13

Liquid Crystalline Copolymers of Monomer-Pairs Containing
Mesogenic Units which Exhibit Constitutional Isomerism

By

Virgil Percec, Jose M. Rodriguez-Parada, Cecilia Ericsson and Hildeberto Nava
Department of Macromolecular Science
Case Western Reserve University
Cleveland, OH 44106-2699

DTIC
ELECTE
AUG 05 1987
S D
C D

Reproduction in whole or in part is permitted for
any purpose of the United States Government.

This document has been approved for public release and sale;
its distribution is unlimited.

87 8 4 05 5

AD A183449

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION / AVAILABILITY OF REPORT Available for publication Distribution unlimited		
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report No. 13			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION Case Western Reserve University		6b. OFFICE SYMBOL (if applicable) 4B566	7a. NAME OF MONITORING ORGANIZATION ONR		
6c. ADDRESS (City, State, and ZIP Code) 2040 Adelbert Road Cleveland, OH 44106			7b. ADDRESS (City, State, and ZIP Code) Office of Naval Research Arlington, VA 22217		
8a. NAME OF FUNDING / SPONSORING ORGANIZATION ONR		8b. OFFICE SYMBOL (if applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER		
8c. ADDRESS (City, State, and ZIP Code) Office of Naval Research 800 N. Quincy Arlington, VA 22217			10. SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO. N00014-86	PROJECT NO. K-0284	TASK NO. 413c024-
					WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) Liquid Crystalline Copolymers of Monomer-Pairs Containing Mesogenic Units which Exhibit Constitutional Isomerism					
12. PERSONAL AUTHOR(S) V. Percec, J. M. Rodriguez-parada, C. Ericsson and H. Nava					
13a. TYPE OF REPORT Preprint		13b. TIME COVERED FROM _____ TO _____		14. DATE OF REPORT (Year, Month, Day)	
				15. PAGE COUNT	
16. SUPPLEMENTARY NOTATION					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP			
			Side-chain thermotropic liquid crystalline polymers		
19. ABSTRACT (Continue on reverse if necessary and identify by block number)					
See attached.					
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION		
22a. NAME OF RESPONSIBLE INDIVIDUAL			22b. TELEPHONE (Include Area Code)		22c. OFFICE SYMBOL

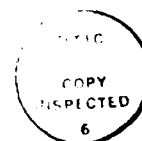
ABSTRACT

✓

The synthesis and characterization of side-chain liquid crystalline copolymers obtained from a monomer pair containing a mesogenic unit which exhibits constitutional isomerism are presented. The particular example described refers to copolymermethacrylates obtained from 4-hydroxy-4'-methoxy- α -methylstilbene and 4-methoxy-4'-hydroxy- α -methylstilbene containing six methylenic units presents a nematic mesophase, while the polymer containing eleven methylenic units presents a smectic A or C mesophase. None of these polymers exhibited side-chain crystallization.

↑

Accession For	
NTIS	CRA&I
DTIC	TAB
Unannounced	
Justification	
By _____	
Distribution/	
Availability Codes	
Dist	Availability Codes
A-1	



Liquid Crystalline Copolymers of Monomer-Pairs
Containing Mesogenic Units which Exhibit Constitutional Isomerism

Virgil Percec, Jose M. Rodriguez-Parada,^{a)}
Cecilia Ericsson^{b)} and Hildeberto Nava

Department of Macromolecular Science
Case Western Reserve University
Cleveland, Ohio 44106
U. S. A.

SUMMARY

The synthesis and characterization of side-chain liquid crystalline copolymers obtained from a monomer pair containing a mesogenic unit which exhibits constitutional isomerism are presented. The particular example described refers to copolymethacrylates obtained from 4-hydroxy-4'-methoxy- α -methylstilbene and 4-methoxy-4'-hydroxy- α -methylstilbene containing six and eleven methylenic units in the spacer. The polymer containing six methylenic units presents a nematic mesophase, while the polymer containing eleven methylenic units presents a smectic A or C mesophase. None of these polymers exhibited side-chain crystallization.

INTRODUCTION

Side-chain liquid crystalline polymers (LCP) containing long spacers and calamitic mesogens undergo side-chain crystallization (1, 2). Copolymerization is most frequently employed to depress the tendency towards crystallization in both main-chain and side-chain LCP (1, 2). Recently, we have developed a novel concept concerning the synthesis of side-chain LC copolymers. It is based on the homopolymerization of a monomer containing a mesogenic unit which undergoes conformational isomerism. Since in both solution or melt the conformational isomers are in a dynamic equilibrium, this homopolymer can be visualized as a "copolymer" obtained from a single monomer. Therefore, the composition of these copolymers is temperature dependent both in solution and in the mesomorphic phase. So far, we were able to suppress side-chain crystallization by using trans-2,5-disubstituted-1,3-dioxane (6), 2,5-disubstituted-1,3,2-dioxaborinane (7), and benzyl ether (8) based mesogenic units.

A slightly different approach to the same problem can be designed by using monomers containing mesogenic units which can give rise to constitutional or structural isomerism. This concept has been of interest both to us (3-5) and to Pino's group (9) in connection with main chain LCP.

The goal of this paper is to present our first results on the synthesis and characterization of side-chain LC copolymers of comonomer pairs containing mesogenic units which are constitutional isomers. Because of our previous experience with 4,4'-dihydroxy- α -methylstilbene based main-chain LC polyethers (3-5), this paper will describe the copolymethacrylates obtained from monomers based on 4-hydroxy-4'-methoxy- α -methylstilbene and 4-methoxy-4'-hydroxy- α -methylstilbene containing eleven and six methylenic units in the spacer.

Present addresses: a) Max-Planck-Institut für Polymerforschung, Postfach 3148, 6500 Mainz, Federal Republic of Germany; b) Department of Polymer Technology, The Royal Institute of Technology, Stockholm, Sweden.

EXPERIMENTAL

A. Materials

All the reagents were commercially available and were used as received, unless otherwise specified. 4,4'-Dihydroxy- α -methylstilbene (HMS) was synthesized and purified according to a method previously developed in our laboratory (10). Its purity was higher than 99.5% as determined by HPLC. m.p. (DSC, 20°C/min), 185°C. 200 MHz $^1\text{H-NMR}$ (DMSO- d_6 -TMS, ppm): 2.2 (-CH₃, s), 6.7 (=CH-, s), 6.85 (4 aromatic protons, o to -OH, d), 7.25 (2 aromatic protons, o to α -CH₃, d), 7.4 (2 aromatic protons, δ to =CH-, d).

B. Synthesis of Monomers and Polymers

Scheme 1 describes the synthesis of the monomers.

Synthesis of 4(4')-Methoxy-4'(4)-hydroxy- α -methylstilbene (I)

4,4'-Dihydroxy- α -methylstilbene (30g, 0.133 mole) was dissolved in a solution of 12.74g (0.32 mole) of NaOH in 120 ml of water. Dimethyl sulfate (12.5 ml, 0.133 mole) was added dropwise, and the solution was stirred at room temperature overnight. The resulting precipitate was filtered and washed with 10% aqueous NaOH, and then with water. The separated solid was dissolved in boiling water and traces of insoluble 4,4'-dimethoxy- α -methylstilbene were separated by hot filtration. The resulting solution was acidified at room temperature with HCl to precipitate the monomethoxylated product. It was filtered, washed with water, and recrystallized from methanol to yield 14.3g (45%) of white crystals. DSC (20°C/min) shows two overlapped broad melting peaks at 139 and 156.6°C, supporting that the resulting compound consists of a mixture of the two constitutional isomers. HPLC (equipped with UV detector) (5, 10), can not discriminate between the two isomers. The chemical shifts of the 200 MHz $^1\text{H-NMR}$ spectrum are presented in Table I.

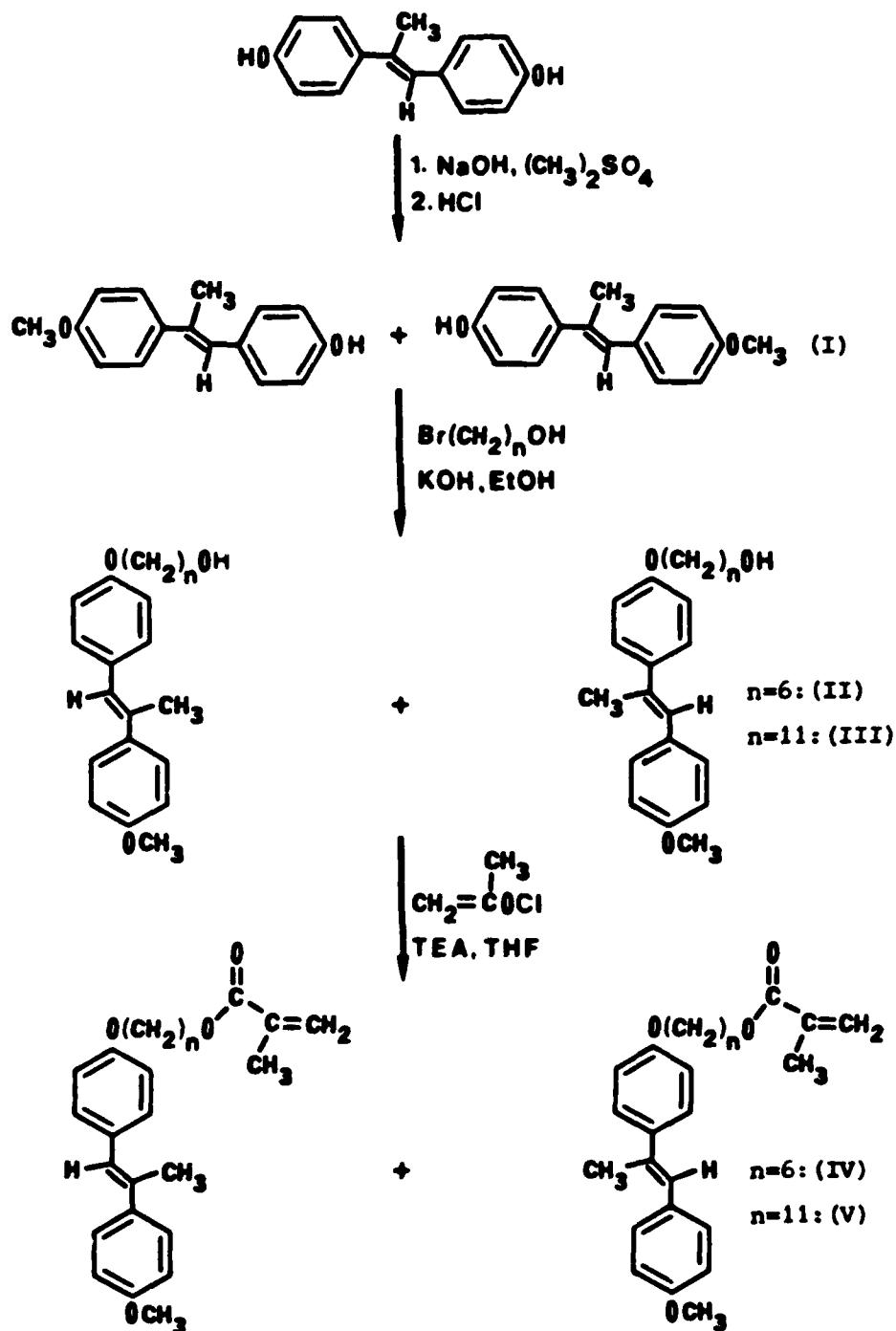
Synthesis of 4(4')-(1-hydroxyhexanyloxy)-4'(4)-methoxy- α -methylstilbene (II) and of 4(4')-(1-hydroxyundecanyloxy)-4'(4)-methoxy- α -methylstilbene (III).

Both compounds were prepared by the etherification of 4(4')-methoxy-4'(4)-hydroxy- α -methylstilbene with 11-bromoundecanol and 6-chlorohexanol respectively, in ethanol at reflux temperature in the presence of KOH as base. An example of this procedure is given below. 4(4')-Methoxy-4'(4)-hydroxy- α -methylstilbene (3g, 0.0125 mole) and KOH (1.05g, 0.0188 mole) were dissolved in 50 ml of 95% ethanol. 11-Bromoundecanol (4.72g, 0.0188 mole) was added and the solution was refluxed for 15 hrs. The reaction mixture was then poured into water and the precipitated product was filtered, washed with dilute solution of aqueous NaOH, water, and recrystallized from methanol to yield 4.65g (90.7%) of white crystals. m.p.=117-119°C. Compound III (61%) has a m.p.=107-109°C. The $^1\text{H-NMR}$ chemical shifts for both compounds are presented in Table I.

Synthesis of Methacrylates IV and V

Both monomers were synthesized by the esterification of the corresponding alcohols (II and III) with methacryloyl chloride. An example follows. III (1.5g, 0.0037 mole) was dissolved in 50 ml of dried THF and 1 ml (0.007 mole) of dried triethylamine was added. The obtained solution was cooled to 0°C in an ice-water bath and 0.5 ml (0.005 mole) of methacryloyl chloride were added dropwise. The reaction was allowed to warm up to room temperature and was kept stirring at this temperature overnight. Finally, it was poured into water, and the precipitated product was filtered, dried, and recrystallized from methanol to yield 1.26g (72%) of white crystals. m.p.=60-85°C (DSC at 20°C/min). Compound IV (65%) presents on its DSC thermogram (20°C/min), two endothermic transitions at 21.6 and 27.5°C, followed by a

nematic mesophase which undergoes isotropization at 46.6°C.



Scheme 1: Synthesis of Monomers

Radical Polymerization of Monomers

Both monomers were polymerized in dried dioxane by using AIBN as a radical initiator at 60°C for 15 hrs. Polymerizations were carried out in Sch-

lenk tubes under an argon atmosphere after the monomer solutions were degassed. The monomer concentration was 10% (w/V) and the initiator concentration was 1 wt% versus the monomer. After the polymerization time, the reaction mixture was diluted with THF and precipitated into methanol. The filtered polymers were dried under vacuum and then purified by reprecipitation from THF solutions into methanol. The characterization of the resulting polymers is presented in Table II.

Table I: Characterization of Monomers and Intermediary Compounds

Compound	Solvent	200 MHz $^1\text{H-NMR}$ (δ , ppm)
I	$(\text{CD}_3)_2\text{CO}$	2.21 (s, $\text{CH}_3\text{-}\overset{ }{\text{C}}=$), 3.11 (s, -OH), 3.80 (s, $\text{CH}_3\text{O-}$), 6.73 (s, HC=), 6.84-7.49 (m, 8 aromatic protons)
II	CDCl_3	1.30-1.87 (m, 4 $\text{-CH}_2\text{-}$), 2.24 (s, $\text{CH}_3\text{-}\overset{ }{\text{C}}=$), 3.65 (t, $\text{-CH}_2\text{OH}$), 3.82 (s, $\text{CH}_3\text{O-}$), 3.97 (t, $\text{-CH}_2\text{OPh}$), 6.72 (s, HC=), 6.85-7.47 (m, 8 aromatic protons)
III	CDCl_3	1.30-1.79 (m, 9 $\text{-CH}_2\text{-}$), 2.24 (s, $\text{CH}_3\text{-}\overset{ }{\text{C}}=$), 3.63 (t, $\text{-CH}_2\text{OH}$), 3.83 (s, $\text{CH}_3\text{O-}$), 3.97 (t, $\text{-CH}_2\text{OPh}$), 6.72 (s, HC=), 6.87-7.47 (m, 8 aromatic protons)
IV	CDCl_3	1.45-1.83 (m, 4 $\text{-CH}_2\text{-}$), 1.94 (s, $\text{CH}_3\text{-}\overset{ }{\text{C}}\text{-COO}$), 2.24 (s, $\text{CH}_3\text{-}\overset{ }{\text{C}}=$), 3.81 (s, $\text{CH}_3\text{O-}$), 3.96 (t, $\text{-CH}_2\text{OPh}$), 4.16 (t, $\text{-CH}_2\text{OOC-}$), 5.54 and 6.10 (s, C=CH_2), 6.72 (s, HC=), 6.85-7.46 (m, 8 aromatic protons)
V	CDCl_3	1.34-1.80 (m, 9 $\text{-CH}_2\text{-}$), 1.93 (s, $\text{CH}_3\text{-}\overset{ }{\text{C}}\text{-COO}$), 2.24 (s, $\text{CH}_3\text{-}\overset{ }{\text{C}}=$), 3.82 (s, $\text{CH}_3\text{O-}$), 3.97 (t, $\text{-CH}_2\text{OPh}$), 4.15 (t, $\text{-CH}_2\text{OOC-}$), 5.53 and 6.08 (s, C=CH_2), 6.72 (s, HC=), 6.86-7.47 (m, 8 aromatic protons)

C. Techniques

The experimental techniques used in the characterization of monomers and polymers i.e., 200 MHz $^1\text{H-NMR}$ spectroscopy, differential scanning calorimetry (DSC), optical polarization microscopy, gel permeation chromatography (GPC), and high pressure liquid chromatography (HPLC) have been previously described (5).

Table II

Radical Polymerization of Monomers and Characterization of the Polymers

Mono-mer	Conv. (%)	$\bar{M}_n \times 10^{-3}$ (GPC) ^{b)}	\bar{M}_w/\bar{M}_n	Thermal Transitions and Thermodynamic Parameters ^{a)}					
				Heating			Cooling		
				Tg	Ti	ΔH_i	Ti	ΔH_i	Tg
IV	79	15.2	2.17	23	113	0.63	108	0.58	19
V	75	15.6	2.17	12	118	2.16	110	2.18	6

a) Tg and Ti are in $^\circ\text{C}$; ΔH_i , in kcal/mru; mru=mole repeat unit.

b) polystyrene standards.

RESULTS AND DISCUSSION

Scheme 1 outlines the synthesis of the two monomers. As we have discussed in the experimental section, the DSC thermograms of the monomethylated 4,4'-dihydroxy- α -methylstilbene have shown two broad overlapped melting

transitions. This result suggests that compound I consists of a mixture containing the two constitutional isomers i.e., 4-methoxy-4'-hydroxy- α -methylstilbene and 4-hydroxy-4'-methoxy- α -methylstilbene. This mixture can be enriched in one of the two isomers by successive recrystallizations from methanol. The analysis of this mixture by 200 MHz $^1\text{H-NMR}$ spectroscopy revealed an almost 50/50 molar ratio between the two isomers.

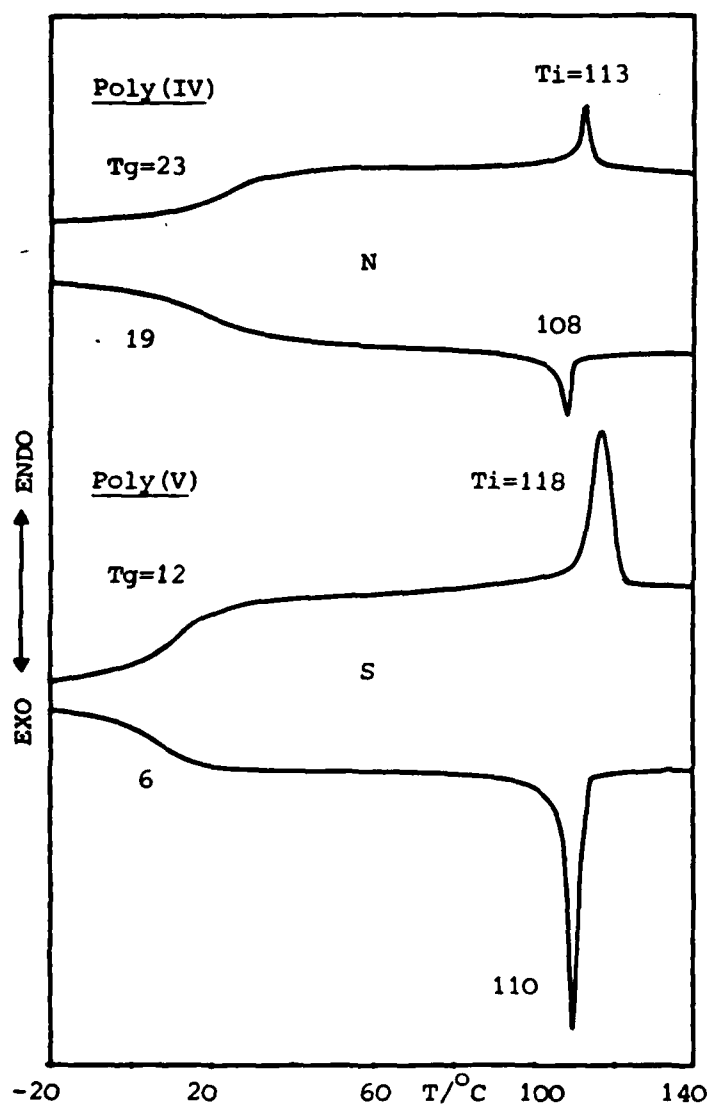
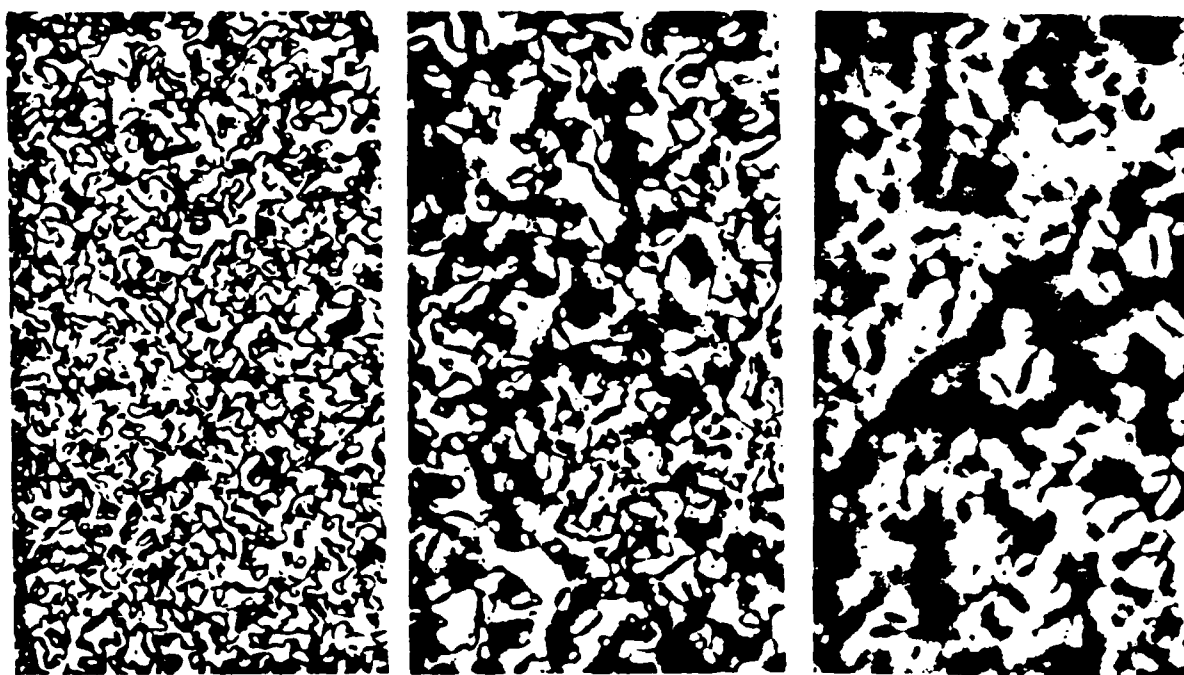


Figure 1: Normalized differential scanning calorimetric thermograms (20°C/min) of: A) Poly(IV), second heating scan; B) Poly(IV), second cooling scan; C) Poly(V), second heating scan; D) Poly(V), second cooling scan.

The DSC thermogram of the monomer IV presents two unidentified endotherms at 21.6 and 27.5°C, followed by a nematic mesophase which undergoes isotropization at 46.6°C. Monomer V presents a broad melting endotherm situated in between 60 and 85°C.

Table II summarizes the radical polymerization of the monomers IV and V and the thermal characterization of the resulting polymers. The number average molecular weights and the polydispersities of the two polymers are quite similar. Therefore, their thermal behavior can be compared in a quantitative way. Typical DSC thermograms for the two polymers are presented in Figure 1. The corresponding thermal transitions and their thermodynamic



A)

B)

C)

Figure 2: Typical optical polarization micrographs (magnification, 300x) of the nematic texture exhibited by Poly(IV): A) after 5 min. at 112°C; B) after 20 min. at 112°C; C) after 40 min. at 112°C.



Figure 3: Typical optical polarization micrographs (magnification, 300 x) of Poly(V): smectic focal-conic texture obtained after 5 hrs of annealing at 118°C.

parameters are listed in Table II. None of these polymers present side-chain crystallization. This could be the consequence of the fact that once the constitutional isomers are attached as polymeric side-groups they suppress the cocrystallization tendency of the side-chains.

Poly(IV) exhibits an enantiotropic nematic mesophase. This assignment is supported by: the low value of the isotropization enthalpy (Table II), its low degree of supercooling (5°C), and the nematic texture observed by optical polarization microscopy (Figure 2).

The isotropization enthalpy of Poly(V) is within the expected values for a smectic mesophase, and at the same time the isotropization transition is supercooled with 8°C (Fig. 1, Table II). Figure 3 presents the focal-conic texture exhibited by poly(V). This texture is characteristic for a smectic A or C mesophase. No definitive assignment for this mesophase is available at this time.

These preliminary results suggest that at least for the examples described here, the copolymerization of two monomers containing mesogenic units which are constitutional isomers, leads to liquid crystalline copolymers which do not undergo side-chain crystallization. A quantitative understanding of these copolymers requires the synthesis, homopolymerization and copolymerization of the individual isomers. Research on this line is in progress in our laboratory.

ACKNOWLEDGEMENTS

Financial support from the Office of Naval Research is gratefully acknowledged.

REFERENCES

1. H. Finkelmann and G. Rehage, *Adv. Polym. Sci.*, **60/61**, 99 (1984)
2. V. P. Shibaev and N. A. Plate, *Adv. Polym. Sci.*, **60/61**, 173 (1984)
3. T. D. Shaffer and V. Percec, *Makromol. Chem., Rapid. Commun.*, **6**, 97 (1985)
4. V. Percec and T. D. Shaffer, in "Advances in Polymer Synthesis", B. Culbertson and J. E. McGrath, Eds., Plenum, New York, 1985, p. 133
5. V. Percec and H. Nava, *J. Polym. Sci: Part A: Polym. Chem.*, **25**, 405 (1987)
6. C. S. Hsu, J. M. Rodriguez-Parada and V. Percec, *J. Polym. Sci: Part A: Polym. Chem.*, in press
7. B. Hahn and V. Percec, *Macromolecules*, submitted
8. C. S. Hsu and V. Percec, *J. Polym. Sci: Part A: Polym. Chem.*, in press
9. R. Deschenaux, P. Neuenschwander and P. Pino, *Helv. Chim. Acta.*, **69**, 1349 (1986)
10. V. Percec, H. Nava and H. Jonsson, *J. Polym. Sci: Part A: Polym. Chem.*, in press

END

9-87

DTIC